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WOLLASTONITE IN SILICATE MATRICES

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Structures of materials with different silicate-based matrices and wollastonite additives as fillers are considered. Dependences of strength and other properties on the quantity and characteristics of wollastonite introduced are analyzed.

Inorganic polymer β -wollastonite β -CaSiO₃ belongs to the group of pyroxenoids, i.e., silicates with a chain structure of silicon-oxygen anions. The chain structure of β -wollastonite is manifested in its fibrous habitus and its splintery fracture. The chemical composition of natural wollastonite is close to pure CaSiO₃, although calcium may be replaced by iron, manganese, or magnesium.

Pseudowollastonite α -CaSiO₃ is a polymorphous modification resistant at a temperature above 1200°C, belongs to the triclinic syngony, produces pseudo-hexagonal forms, and significantly differs from β -CaSiO₃ in its properties.

The density of α -CaSiO₃ is 3.09×10^3 kg/m³, that of β -CaSiO₃ is 2.87×10^3 kg/m³ [1]. At 1125°C wollastonite irreversibly transforms into pseudowollastonite with insignificant volume variations. The melting point is 1540°C, Mohs hardness 4.5–6.0, the TCLE of α -CaSiO₃ is 11.8×10^{-6} K⁻¹, and the TCLE of β -CaSiO₃ is 6.5×10^{-6} K⁻¹.

The areas of application of wollastonite are diverse [2] due to its needle-shaped morphology, a low TCLE, and high refractive index and whiteness parameter. The use of wollastonite as a source for calcium oxide is lately decreasing (Table 1).

The needle shape of wollastonite crystals determines its application as a reinforcing filler in composite materials with different matrices, including an alternative to asbestos, since wollastonite is not carcinogenic, in contrast to asbestos.

The reinforcement of composite materials with the needle-shape phase increases destruction viscosity, resistance to thermal shocks, and strength of matrix by increasing work done against destruction and by impeding crack propagation on the matrix boundary, as well as by microcracking in the crack apex zone and changing the crack path. Used in compositions of paints, the needle-laminar shape of wollastonite crystals improves the coverage and strength parameters of coatings and allows for substantial saving of pigments.

The efficiency of fiber reinforcement depends on the ratio of crystal length l to its diameter d , the volume content of fibers, and the strength of their bond with the matrix. An increase in the ratio l/d usually improves the strength properties of materials, but this ratio, a rule, has an optimum. Thus, reinforcing a dense ceramic matrix by filament crystals, it is regarded that about 20 vol.% crystals is the optimum ratio [3].

To obtain a high-strength material with a brittle matrix, the fibers should not adhere too strongly to the matrix. In this case when a crack emerges and propagates, the mechanism of “drawing fibers out of the matrix” is implemented [4], where the work required for destruction grows and the elastic component of mechanical strength of material increases. An example of a composite material with low adhesion of fiber to matrix is asbestocement (Fig. 1).

A deviation from stoichiometry takes place in formation of wollastonite due to a difference in diffusion mass transfer velocities, which is typical of synthesis of a complex oxide from simple oxides [5]. Since the rate of diffusion mass

TABLE 1

Application area	Application purpose	Share in total consumption, %	Tendency of application
Ceramics	Source of calcium oxide and reinforcing material	40–45	Decreases
Plastics	Reinforcing filler	20–25	Increases
Building, sealing and friction materials	Replacement of asbestos	20–25	The same
Metallurgy	Heat insulation resistant to melts of aluminum and nonferrous metals	About 10	“
Paints and other sectors	White-color filler decreasing pigment consumption	About 5	“

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transfer is higher in calcium cation than in silicon, at first a solid solution of SiO_2 in CaSiO_3 is formed, while the remaining CaO is concentrated near crystal surface (pH of wollastonite suspension is 8–9). An assumption exists that when wollastonite is used in lining in metallurgy, it is calcium oxide that facilitates fast oxidation of aluminum and the formation of an aluminum oxide film preventing further reaction between wollastonite ceramics and metal melt [6].

Our study considered the structure and properties of composite materials based on cement, hydrosilicate, and glass-ceramic matrices reinforced by needle-shaped crystals of natural β -wollastonite. The samples were investigated using a Hitachi S405A electron microscope and a MIN-8 optical microscope. We determined the bending and compression strength of samples and some properties that are specific for different materials (water demand, water absorption, linear shrinkage, etc.). The characteristics of wollastonite varieties used in the study are listed in Table 2.

Samples of different compositions were made using batch-preparation and molding methods typical of each specified material. Thus, composite materials with a calcium hydrosilicate matrix reinforced with wollastonite (up to 70%) were produced from a mixture of diatomite from the Inzenskoe deposit and quick lime with a component ratio corresponding to the composition of wollastonite. Samples based on cement had additives of wollastonite (up to 15%), microsilica, and various plasticizers. Samples with a ceramic matrix had a composition containing over 50% clay, quartz sand, feldspar, and dolomite. Wollastonite in an amount of up to 15% was introduced into the mixture to replace dolomite.

The presence of a predominant orientation (texturing) in composite materials with additives of anisotropic particles has a great effect on their strength properties. The emergence of anisotropy in structures to a large extent depends on the method of batch preparation and molding of material.

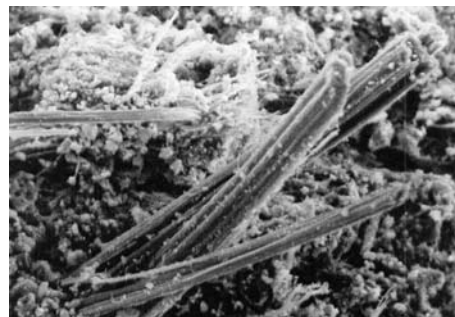


Fig. 1. Structure of cement stone with asbestos fibers (virtual absence of interaction between the matrix and fiber).

Heat insulation samples based on wollastonite were produced by moist paste mixing and molded by casting in gypsum or metal molds. Next, the samples were subjected to autoclave treatment and firing for the purpose of transforming a hydrosilicate matrix into wollastonite. A relatively high viscosity of the molding mixture and moderate molding force did not produce any clearly defined textures.

Samples based on a cement binder were molded by various methods: compression, casting, and extrusion. Hardening of samples was implemented by steam-curing. The degree of texturing of samples was different in different molding methods.

Samples based on clays were prepared by granulation and subsequent molding, drying, and firing. The orientation of the wollastonite particles introduced was not prevalent, since wollastonite crystals reinforce granules, which impedes their deformation and consolidation of the molded product during compression.

Analysis of the microstructures of materials obtained indicates that asbestos and wollastonite particles react differently to the matrices. The lowest degree of interaction be-

TABLE 2

Parameter	Wollastonite									
	M-075	M-100	M-300	VK-2	VK-3	WIC-10PA	WIC-10	WIC-40	FW-200	FW-325
Average particle size, μm	8	43	46	37	15	11	11	20	8	6
Ratio l/d	2	4	3	6	5	4	5	6	2	2
Fraction content, %, based on length, μm :										
315 – 200	0.4	0	2.7	1.4	0	0	0	0.3	0	0
200 – 100	0.5	7.9	8.2	8.3	0.7	0	0.2	1.1	0	0.2
100 – 71	0.3	15.7	2.8	4.1	3.7	0.2	0	1.4	0.6	0.7
71 – 45	1.5	9.8	6.9	5.5	3.7	0.7	1.3	6.1	1.1	0.9
45 – 20	6.0	33.3	26.0	50.3	30.9	15.1	15.3	36.1	11.9	3.7
20 – 10	10.2	33.3	26.0	17.3	13.2	31.7	45.4	27.2	15.6	9.3
10 – 5	11.9	0	27.4	13.1	14.7	37.3	37.8	27.8	14.2	29.6
5 – 0	69.2	0	0	0	33.1	15.0	0	0	56.6	55.6
Specific surface area, m^2/kg , based on readings:										
of PSKh-2 instrument	365.1	92.6	< 50.2	195.7	393.7	595.2	667.9	375.8	350.2	677.8
of laser granulometer	228.2	71.1	73.1	151.3	334.8	535.8	556.1	328.4	302.9	490.1

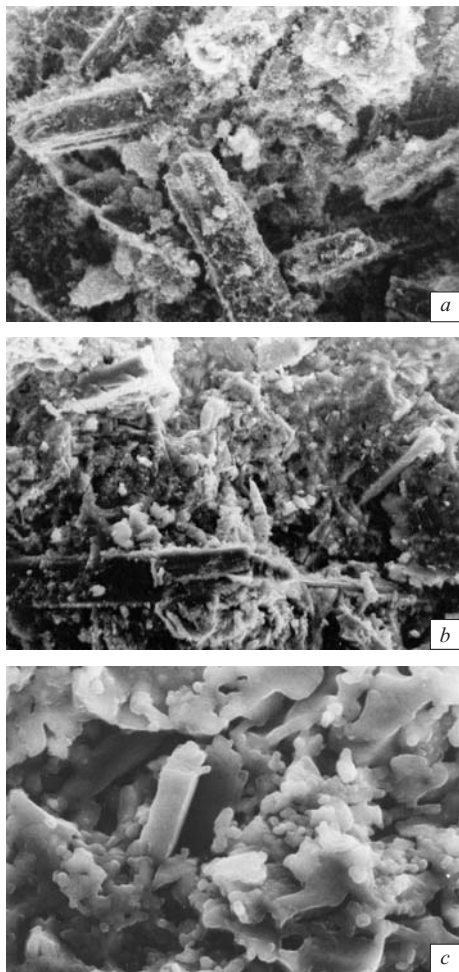


Fig. 2. Microstructure of heat insulation samples (a), cement stone (b), and sintered ceramics based on tile mixture (c).

tween an additive and a matrix is observed in asbestocement, in which asbestos fibers (fibrils) located in a porous matrix can be torn out when a sample breaks, which can be seen in its fracture (Fig. 1).

The microstructure of the heat insulation sample based on the hydrosilicate binder contains many randomly located wollastonite crystals, whose surface is coated by a loose layer of fine particles of dehydrated calcium silicate, partly transformed into weakly crystallized wollastonite (Fig. 2a).

The microstructure of cement stone with a wollastonite additive is characterized by a substantial quantity of new hydrate formations on the surface of wollastonite crystals and a sufficiently high degree of cohesion between the matrix and the reinforcing filler (Fig. 2b). The pores in this material have the size below 10 μm , and the structure itself is much denser than the structure of the heat-insulation sample.

Introduction of wollastonite into the glass-ceramic matrix of clay-based ceramics reinforces the matrix by fibrous and laminar wollastonite particles (Fig. 2c). The quantity of the vitreous phase (8–15%) depends both on impurities present in wollastonite and on the degree of interaction of

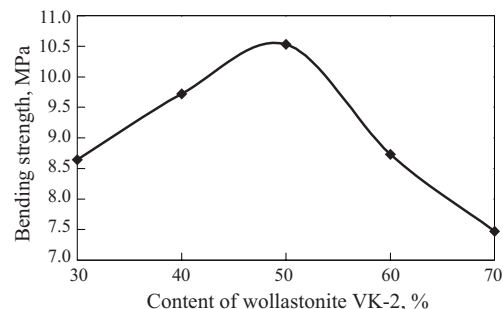


Fig. 3. Bending strength of material with a lime-silica matrix depending on wollastonite VK-2 content.

wollastonite particles with the aluminosilicate matrix, which is manifested in pores of a predominantly oval or elliptical section with smooth rounded walls. Some wollastonite particles are completely surrounded by pore space, which is presumably a result of partial dissolution of wollastonite surface and distribution of the emerging glass in the surrounding material. Some of wollastonite particles are seen to retain their habitus.

The specifics of microstructure of the materials obtained were most clearly observed in a relationship between the mechanical strength of samples and the quantity of wollastonite introduced.

Judging from strength parameters, the optimum content of wollastonite of different grades in heat-insulating materials ranges from 30 to 50%. The higher the dispersion of wollastonite and the greater the ratio l/d , the lower is the quantity of wollastonite that should be added, which is related to an increasing water demand of mixtures. The dependence of mechanical strength on the content of wollastonite, as a rule, has an extremum. The maximum values (Fig. 3) were obtained adding wollastonite VK-2 (40%): compressive strength 15 MPa, bending strength 11.8 MPa (volume mass 0.9 kg/cm^3). A more fibrous wollastonite of grade WIC-10PA did not fully display its properties, since it has a very high specific surface area (over 500 m^2/kg) and, consequently, a higher water demand.

It should be noted that the bending strength of wollastonite heat-insulating samples differs insignificantly from its compression strength, i.e., the reinforcing effect is clearly observed.

Analysis of studying the effect of various grades of wollastonite on water demand of samples in molding and shrinkage in firing indicates that introduction of wollastonite M-300 (average particle size 46 μm with a low l/d ratio equal to 3) to a maximum extent facilitates a decrease in the water-to-solid ratio due to a decreased content of the hydraulic binder. On adding 50% wollastonite, the linear shrinkage of samples significantly decreases after the formation of a spatial skeleton (percolation cluster). At the same time, even with such a low l/d ratio, the reinforcing effect of wollastonite is observed. The strength parameters have maximums

and nearly always coincide in samples containing about 50% wollastonite (compressive strength 11 MPa, bending strength 10 MPa).

With small sizes of wollastonite particles (in WIC-10PA the mean particle size is 11 μm , $l/d = 4$, in WIC-40 the mean size is 20 – 40 μm , $l/d = 6$), a difference in their effect on the properties of samples is manifested clearly enough, being especially perceptible in flow properties of the molding mixture. Wollastonite WIC-10PA decreases the water-solid ratio more significantly than WIC-40. It is possible that the particles of wollastonite WIC-10PA are close in size to the size of the binder particles. In this case the effect of ratio l/d is less evident and the system in its behavior approaches a system with isometric particles. However a decrease in the water – solid ratio in this case is half as much as in the case of large isometric particles in wollastonite M-300.

The relationships of compressive strength in samples containing wollastonite WIC-40 and WIC-10PA are of a similar nature, but in wollastonite WIC-10PA the sharp drop in strength is shifted toward a higher content of the filler. This is related to the formation of the structure consisting of continuous filler clusters.

Modifications of structure in sintering to a larger extent occur in samples with higher shrinkage (containing wollastonite WIC-40). The bending strength of these samples varies less with an increasing filler content than in samples with wollastonite WIC-10PA. For the latter, strength variations have a different character. When a wollastonite content is equal to 50%, an anomaly related to the formation of the infinite filler cluster is manifested.

An intermediate position with respect to strength variations, but closer to samples with wollastonite M-300 is taken by samples with filler VK-2 (mean particle size is 37 μm , $l/d = 6$). The large size of wollastonite particles results in the fact that as the filler content grows, the water-solid ratio decreases more significantly than in mixtures with wollastonite WIC-40 and WIC-10PA. The course of this curve is close to the curve for mixtures with additives of wollastonite M-300.

Relationships of the compressive and bending strength parameters for samples with wollastonite VK-2 are close to those for samples with M-300. Dependences of shrinkage of samples containing wollastonite M-300 and VK-2 differ significantly, which is a consequence of a higher content of larger particles in wollastonite M-300 (wollastonite M-300 contains twice as much particles of size 315 – 200 μm). Accordingly, with a rather coarse filler, the size of its particles has the primary significance, and not the ratio l/d . A decreased density of articles containing particles with a higher l/d ratio is compensated by their reinforcing effect.

The above regularities are manifested using a portland-cement matrix as well. Mass transfer in molding in such matrix is significantly less intense than in sintering. It is interesting, that using wollastonite VK-2, the maximum strength was registered when its content was 20%, which, considering the proximity of densities of the matrix and

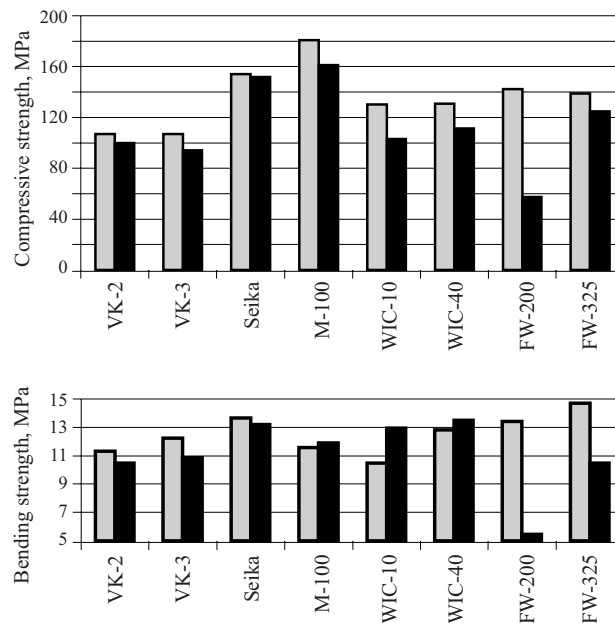


Fig. 4. Compressive and bending strength of samples of cement with additives of various grades of wollastonite. Molding pressure: □) 30 MPa; ■) 20 MPa.

wollastonite is very close to the optimum content of fibers in reinforcing dense ceramic matrices [3]. The study of sample fractures showed that in contrast to asbestos-containing samples, no effect of “drawing fiber out of matrix” is seen here. There is another maximum, when the content of wollastonite is equal to 40 – 50%, which is presumably related to the formation of a continuous cluster skeleton consisting of wollastonite crystals. Water demand in this case increases nearly linearly with increasing content of wollastonite, although it decreases in the calcium hydrosilicate matrix. This is presumably due to a very high water demand of the components of the lime-diatomite binder.

The use of molding methods ensuring the maximum orientation of fibers (suction of cement-wollastonite pastes using PVA as plasticizers and subsequent additional compression) made it possible to obtain samples with bending strength not inferior to the traditional asbestos-cement materials. Random orientation of particles in using semidry molding of a cement-wollastonite mixture made it possible to ensure high density and compressive strength, but its bending strength was significantly lower than in asbestos-cement samples (Fig. 4).

Wollastonite of various grades added to ceramic mixtures has a different role. Wollastonite in the molding and drying stages acts as a filler improving the molding and drying properties, and in high-temperature firing it participates in liquid-phase sintering as a flux (at temperatures above 1000°C) and simultaneously in the case of low activity of the matrix increases deformation resistance in firing.

Ceramic samples with wollastonite additives, in contrast to ceramics without additives, in testing do not exhibit a pro-

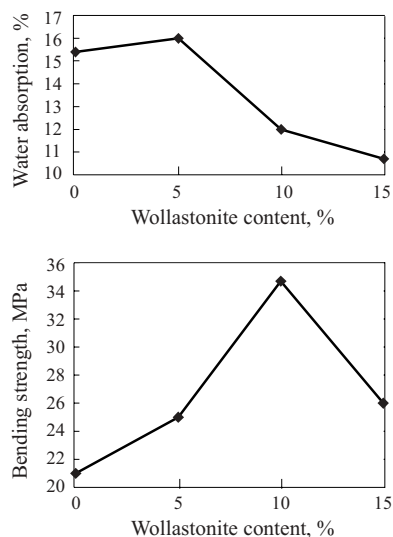


Fig. 5. Dependence of water absorption and bending strength of ceramic samples on a content of wollastonite M-100.

portional correlation between the porosity of sintered samples (water absorption) and their mechanical strength, which is due to the reinforcing effect of wollastonite particles (Fig. 5).

The presence of a maximum on the dependence of strength of ceramic on the content of wollastonite M-100 shows a clearly expressed reinforcing effect in material. With a low l/d ratio and the mean particle size (length) slightly over 30 μm , wollastonite of this grade has a low specific surface area and, accordingly, low surface activity. Figure 2c shows the microstructure of ceramics with wollastonite M-300 additive, which has even lower parameters of the average size, ratio l/d , and specific surface area, than wollastonite M-100. It can be seen that some wollastonite crystals virtually have not changed. In general, a high firing temperature leads to the formation of a eutectic glass melt on the surface of wollastonite crystals and its partial dissolution in the matrix.

Thus, the effect of wollastonite of various grades on properties of ceramic samples is more difficult to estimate than in the case of the lime-silica and cement matrices. It is necessary to take into account not just the activity of wollastonite particles (particle size and specific surface area), but also interaction of the matrix with wollastonite.

The following conclusions can be drawn from the studies performed.

Interaction between wollastonite and the matrix has a crucial influence on the reinforcing effect of wollastonite. An excessive increase in the strength of its bond with the matrix weakens the reinforcing effect (increases a spread between the values of bending and compression strength).

An increase in wollastonite content modifies structure, which is related to the formation of an infinite cluster consisting of filler particles (filler particles contacts each other). Similarly to spherical particles, this occurs when the content of filler is 40 – 50% (the properties change depending on a content of the filler).

The size of particles, especially of large ones, and the ratio l/d have a great effect on the properties of the cluster formed.

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